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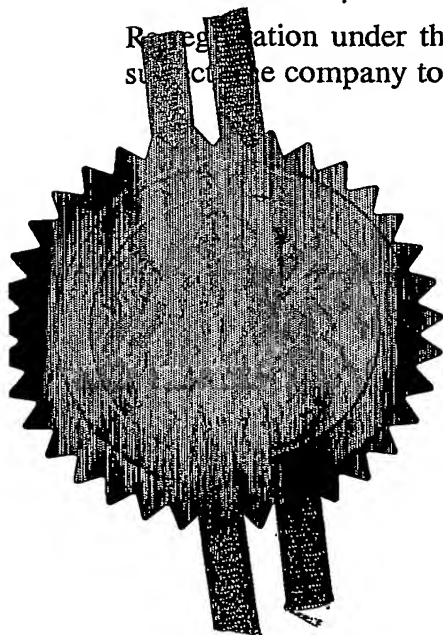
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1. Your Reference

P58938V-RR

M03317763/AS3

2. Patent Application number
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0323417.6

(-7 OCT 2003)

3. Full name, address and postcode of the or each applicant (underline all surnames)

The BOC Group plc
Chertsey Road
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GU20 6HJ

Patents ADP Number (if you know it)

7975949001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

Electrochemical Sensor

5. Name of your agent (if you have one)

FRY HEATH & SPENCE LLP

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to which all correspondence should be sent
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Country

Priority application
number
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Date of filing
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application.

Number of earlier application

Date of filing
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor; or
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Statement of inventorship and right to grant of a patent (Patents Form 7/77) 0

Request for preliminary examination and search (Patents form 9/77) 1

Request for substantive examination (Patents form 10/77) 0

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11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

Victoria Townsend

7 October 2003

12.

Name and daytime telephone number of person to contact in the United Kingdom

Andrew Booth 01276 807612
Victoria Townsend 01293 776800

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Duplicate

Electrochemical Sensor

The current invention relates to sensors for the detection of organic
5 contaminants in low oxygen concentration process environments such as
those used in the semiconductor manufacturing industry, the use of such
sensors and a novel method for the detection of organic contaminants in
such process environments. By the term low oxygen concentration
process environments it is to be understood to mean process
10 environments in which the partial pressure of oxygen is of the order of 10^{-6} mb – 10^{-3} mb (parts per billion to parts per million).

In, for example, the semiconductor manufacturing industry, it is
important to control the atmosphere (process environment) in which
15 wafers are manufactured. The wafers are desirably manufactured in a
controlled environment. Undesirable or varying levels of organic
contaminants can result in device and/or equipment failure.

Levels of contaminating organic material in the parts per trillion
20 (ppt) to parts per billion (ppb) range, which corresponds to a partial
pressure of 10^{-9} to 10^{-6} mb do not, in general, result in equipment or
device failure. However, if the levels of organic contaminants become
much higher than this, failures may result. In order to control the process
environment, it is necessary to monitor the levels of organic contaminants
25 present. In particular, some processes are sensitive to contaminant
material in the low ppb range, it is therefore desirable to monitor the level
of contaminant materials in the ppt range for such processes. However,
such monitoring processes are costly and it is difficult to determine an
accurate value for the total organic compounds (TOC) present at such low
30 contaminant levels. In addition, many fabrication processes are tolerant of
light saturated hydrocarbons such as methane (CH_4) and ethane (C_2H_6),
which have a particularly low reaction probabilities with most surfaces and
therefore do not take part in the various contamination inducing reactions.

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In vacuum based process environments, TOC levels are often determined using mass spectrometry. A mass spectrometer is capable of measuring contaminants present at ppt levels. However the interpretation of such measurements is often complicated by effects such as mass spectral overlap, molecular fragmentation and background effects, for example.

Although mass spectrometers can be used in process environments operating at ambient pressure or above, additional vacuum and sample handling systems are required, which make such instruments very expensive. Under such conditions, it is preferred to use Gas Chromatographic (GC) techniques to monitor the TOC levels present in the process environment. However, in order to monitor contaminants in the ppt range it is necessary to fit the gas chromatogram with a gas concentrator. Gas Chromatography technology can therefore be used to monitor TOC levels in the ppt range in Ultra High Purity (UHP) gas installations in semiconductor fabrication plants.

It should be noted that although Mass Spectrometry and Gas Chromatography are able to detect ppt levels of TOC, their ability to differentiate the presence of the process tolerant light hydrocarbons referred to above from the more harmful organic compounds is limited, which makes it difficult to determine the total levels of damaging hydrocarbons in the process environment.

In addition, because the use of either mass spectrometric or gas chromatographic techniques for determining the TOC levels present in process environments requires specialist equipment, they tend to be rather expensive and are typically only used as Point of Entry (POE) monitors for the whole facility rather than the more useful Point of Use (POU) monitors.

Hydrocarbons, including light hydrocarbons such as methane (CH_4) and ethane (C_2H_6), have been routinely monitored using common tin oxide (SnO_2) based sensor devices. These sensors typically operate under atmospheric pressure to detect target gases in the range from 10s of ppb (parts per billion) to several thousand ppm (parts per million). This type of sensor works effectively within these ranges by providing a linear output signal that is directly proportional to the quantity of target gas within the monitored environment. Although these sensors are suitable for monitoring contaminant levels within ambient environments, they do not lend themselves for applications with sub-atmospheric processing environments such as those encountered within semi-conductor processing environments. However, under such vacuum conditions the SnO_2 type of sensor (typically used for monitoring hydrocarbon levels in ambient) will suffer from reduction of the active oxide content leading to signal drift and non-response after a period of time.

Chemical sensors comprising solid state electrolytes such as oxygen anion conductors or silver or hydrogen cation conductors have been used to monitor levels of oxygen and carbon dioxide and hydrogen / carbon monoxide gas present in a process environment and are described in United Kingdom patent application number 0308939.8 and GB 2,348,006A, GB 2,119,933A respectively.

Such sensors are generally formed from an electrochemical cell comprising a measurement electrode, a reference electrode and a solid state electrolyte of a suitable ionic conductor disposed between and bridging said electrodes.

The gas monitor of GB 2,348.006A comprises a detection electrode containing a silver salt having an anion, which corresponds to the gas to be detected, a silver ion conducting solid state electrolyte and a reference silver electrode. The monitor can be used to detect gases such as carbon

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dioxide, sulphur dioxide, sulphur trioxide, nitrogen oxides and halogens through the suitable choice of the appropriate anion.

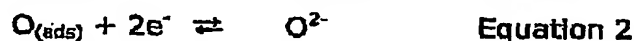
For the oxygen sensors of United Kingdom patent application
 5 number 0308939.8, the solid state electrolyte conducts oxygen anions and the reference electrode is generally coated or formed from a catalyst, which is able to catalyse the dissociative adsorption of oxygen and is positioned within a reference environment, in which the concentration of oxygen adjacent the reference electrode remains constant.

10

Solid state oxygen anion conductors (solid state electrolytes) are generally formed from doped metal oxides such as gadolinium doped ceria or yttria stabilised zirconia (YSZ). At temperatures below the critical temperature for each electrolyte (T_c) the electrolyte material is non-
 15 conducting. At temperatures above T_c the electrolyte becomes progressively more conductive.

The levels of oxygen determined by such oxygen sensors in any monitored environment is determined by the electrochemical potentials
 20 generated by the reduction of oxygen gas at both the measurement and reference electrodes. The steps associated with the overall reduction reactions at each electrode are set out below, the half-cell reaction at each electrode being defined by equations 1 and 2 below.

25



The electrochemical potential generated at each electrode is determined by the Nernst equation:

$$E = E^\ominus + \frac{RT}{2F} \ln \frac{a(O_{ads})}{a(O^{2-})} \quad \text{Equation 3}$$

Where

E is the electrochemical half-cell potential at the reference or measurement electrode respectively;

E^\ominus is the standard electrochemical half cell potential of the cell at unit $O_{(ads)}$ activity

R is the gas constant

T is the temperature of the cell

F is Faraday's constant

$a(O_{ads})$ and $a(O^{2-})$ are the activities of the adsorbed oxygen at the electrode surface and reduced oxygen anion in the solid state ionic conductor respectively.

The activity of adsorbed oxygen at the electrode surface is directly proportional to the partial pressure of oxygen gas in the environment adjacent the electrode as defined by equation 4 below:

$$a_{O_{ads}} = K P_{O_2}^{1/2} \quad \text{Equation 4}$$

Since $a(O^{2-})$ is unity, by definition, and the activity of the adsorbed oxygen at the electrode surface is proportional to the partial pressure of the oxygen in the environment adjacent the electrode surface (Equation 4), the half cell potential can be written in terms of the partial pressure of

$$E = E^\ominus + \frac{RT}{4F} \ln P_{O_2} \quad \text{Equation 5}$$

oxygen in the particular environment adjacent the measurement or reference electrode respectively (Equation 5).

Where

E is the electrochemical half-cell potential at the reference or measurement electrode respectively;

E^\ominus is the standard electrochemical half cell potential of the cell for oxygen at atmospheric pressure i.e. unit activity;

R is the gas constant

6

T is the temperature of the cell

F is Faraday's constant; and

$P(O_2)$ is the partial pressure of oxygen gas in the environment adjacent the electrode surface.

5

The potential difference V generated across the cell is defined in terms of the difference in the half-cell potentials between the reference and measurement electrodes in accordance with Equation 6.

$$V = E_{(R)} - E_{(M)} = \frac{RT}{4F} \ln \left(\frac{P_{O2(R)}}{P_{O2(M)}} \right) \quad \text{Equation 6}$$

10

Where

V is the potential difference across the cell

$E_{(R)}$ and $E_{(M)}$ are the electrochemical potentials at the reference and measurement electrodes respectively;

R, T and F are as defined above; and

15

$P_{O2(R)}$ and $P_{O2(M)}$ are the partial pressures of oxygen at the reference and measurement electrodes respectively.

Note that if both the reference and measurement electrodes are exposed to the same oxygen partial pressure e.g. atmospheric levels of oxygen, the potential difference across the cell is zero.

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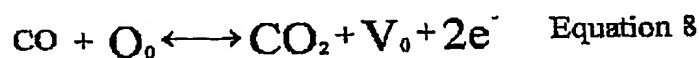
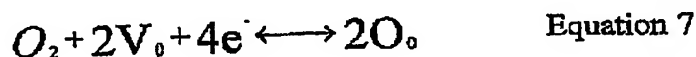
However, in process environments such as the oxygen deficient environments encountered in the manufacture of semi-conductor products the partial pressure of oxygen adjacent the measurement electrode is considerably less than that adjacent the reference electrode. Since the electrochemical potential at each electrode is governed by the Nernst equation, as the partial pressures of oxygen at the measurement electrode decreases, the electrochemical potential at the measurement electrode changes, which results in the formation of a potential difference across the cell at temperatures above the critical temperature. The potential difference across the cell is determined by the ratio of the partial

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pressure of oxygen at the reference and measurement electrodes in accordance with equation 6 above. The oxygen sensor can therefore provide a user with an indication of the total amount of oxygen present in a monitored environment simply from determining the potential difference
5 across the cell.

Reducing gases such as hydrogen, carbon monoxide, nitrous oxides and hydrocarbons present in oxygen rich environments (% levels of oxygen) such as automobile exhaust gases, for example can be detected
10 using mixed potential sensors. Such sensors comprise a solid state oxygen anion conductor electrolyte having dissimilar catalytic electrodes formed on one surface thereof. The sensor response results from the development of an equilibrium mixed potential difference between the catalytically dissimilar electrodes in the presence of the reducing gas as outlined for
15 example in DE95/00255 where the dissimilar catalytic reactions are enhanced by operating the electrodes at different temperatures. The mixed potential for a particular electrode surface arises from the competition between the electrochemical reduction of oxygen (equation 7) and the oxidation or combustion of the organic / reducing material
20 arriving at the electrode surface (e.g. for carbon monoxide equation 8).



Where V_o is a doubly charged oxygen anion vacancy and O_o is a
25 filled oxygen anion site in the oxygen anion conducting solid state electrolyte.

Since the carbon monoxide, for example, is oxidised at the surface of one of the electrodes only (the catalytically active one), adsorbed
30 oxygen is consumed at that electrode and the electrochemical potential at

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the active electrode increases as a result. The other electrode is catalytically inactive and oxidation of the carbon monoxide does not occur here. This means that the concentration of adsorbed oxygen at the surface of this electrode remains constant and is independent of the carbon monoxide partial pressure. This is reflected by the measured electrochemical potential at that electrode. The difference in electrochemical potentials between the active and inert electrodes is a reflection of the difference in equilibrium amounts of adsorbed oxygen present at the surface of the electrodes. The amount of carbon monoxide in the atmosphere can therefore be determined from the equilibrium potential voltage. These mixed potential sensors provide a good indication of the concentration of reducing gases present in the monitored environment if the environment is rich in oxygen (% levels of oxygen). However, they are unsuitable for use in environments containing little or no oxygen.

There is therefore a need for a simple, low cost, semi-quantitative sensor, which has a low sensitivity to unreactive organic compounds but can be used at the point of use to analyse oxygen deficient process environments. The present invention addresses that need.

A first aspect of the present invention provides an organic contaminant molecule sensor, for use in a low oxygen concentration monitored environment the sensor comprising an electrochemical cell having:

a solid state oxygen anion conductor having a first and a second surface, wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;

an active measurement electrode formed on the first surface of said solid state oxygen anion conductor, the active measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the oxidation of an organic contaminant molecule to carbon

dioxide and water at the surface thereof, the electrode being positioned for exposure to the monitored environment;

an inert measurement electrode formed on the first surface of the solid state oxygen anion conductor adjacent to and independent of the active measurement electrode, the inert measurement electrode being
5 coated with or formed from a material, which is catalytically inert to the oxidation of an organic contaminant molecule at the surface thereof, the electrode being positioned for exposure to the monitored environment;

a reference electrode formed on the second surface of the solid
10 state oxygen anion conductor, the reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociative adsorption of oxygen, the reference electrode being positioned within a reference environment;

means for controlling and monitoring the temperature of the cell at
15 a temperature at or above the critical temperature, T_c , of the oxygen anion conductor ;

sealing means for separating the reference environment from the monitored environment;

means for controlling the electrical currents, I_a and I_i , flowing
20 between the reference electrode and the active and inert measurement electrodes respectively, thereby to control the flux of oxygen anions flowing between the reference electrode and the active and inert measurement electrodes respectively; and

means for monitoring the potential difference between the
25 reference electrode and the active measurement electrode (E_a) and between the reference electrode and the inert electrode (E_i) and therefore the potential difference V_{sense} between the active measurement electrode (E_a) and the inert electrode (E_i);

whereby in the absence of organic contaminant molecules the
30 potential difference V_{sense} between the active and inert measurement electrodes assumes a base value V_b and in the presence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes assumes a measurement value V_m , the

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value $V_m - V_b$ being indicative of the concentration of organic contaminant molecules present in the monitored environment.

5 In another aspect, the invention is An organic contaminant molecule sensor for use in environments having high oxygen concentrations, the sensor comprising an electrochemical cell having:

an oxygen anion conductor wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;

10 an active measurement electrode in contact with the oxygen anion conductor, the active measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the oxidation of an organic contaminant molecule to carbon dioxide and water at the surface the electrode being positioned for exposure to the monitored environment;

15 an inert measurement electrode in contact with the oxygen anion conductor independent of the active measurement electrode, the inert measurement electrode being coated with or formed from a material, which is catalytically inert to the oxidation of an organic contaminant molecule at the surface the electrode being positioned for exposure to the monitored environment;

20 a reference electrode in contact with the oxygen anion conductor, the reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociative adsorption of oxygen, the reference electrode being positioned within a reference environment;

25 means for controlling and monitoring the temperature of the cell at a temperature at or above the critical temperature, T_c , of the oxygen anion conductor;

sealing means for separating the reference environment from the monitored environment;

30 means for controlling the electrical currents, I_a and I_i , flowing between the reference electrode and the active and inert measurement electrodes respectively, thereby to control the flux of oxygen anions flowing between the reference electrode and the active and inert

measurement electrodes respectively such that the NEMCA effect is activated; and

means for monitoring the potential difference between the active measurement electrode (E_a) and the inert electrode (E_i) whereby in the absence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes assumes a base value V_b and in the presence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes assumes a measurement value V_m , the value $V_m - V_b$ being indicative of the concentration of organic contaminant molecules present in the monitored environment.

In the absence of organic contaminants, the potential difference between the active and inert measurement electrodes is constant and is determined by the differences in the catalytic rate of recombination and desorption of oxygen from the surfaces of the active and inert measurement electrodes respectively as influenced by the currents I_a and I_i flowing between the reference electrode and the active and inert measurement electrodes respectively. However, when organic contaminants are introduced into the process environment, they are catalytically oxidised at the surface of the active measurement electrode and the concentration of adsorbed oxygen at the surface of the active measurement electrode decreases. This means that, in accordance with equation 3 above, the potential difference, V_{sense} , between the active and inert measurement electrodes increases to a value V_m . By suitably calibrating the monitor, the difference $V_m - V_b$ between the potential differences in the presence and absence of organic contaminant molecules can be used to determine the concentration of organic contaminant molecules in the process environment.

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It should be noted that the provision of means for controlling the electrical currents, I_a and I_i , flowing between the reference electrode and the active and inert measurement electrodes respectively, thereby to

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control the flux of oxygen anions flowing between the reference electrode and the active and inert measurement electrodes respectively allows the sensor to determine low levels of organic contaminant in low oxygen concentration environments. The provision of currents I_a and I_i flowing
5 between the active and inert electrodes respectively provides a source of oxygen at the surface of each of the electrodes. The provision of such an oxygen source is particularly important at the surface of the active electrode since it provides a source of oxygen for reaction with the organic
10 contaminant at the surface of that electrode. This is important since it means that the response of the sensor does not rely on the presence of oxygen gas in the sensing atmosphere itself. The sensor can therefore be used to provide a semi-quantitative indication of the presence of organic
15 material by measuring a parameter which depends upon the difference in the catalytic rates of oxidation occurring between the active and inert sensing electrodes - usually the potential difference between the active and inert electrodes relative to the reference electrode.

In use the sensor operates by passing a small anion current, I_a (O^2), between the reference electrode and one of the sensing electrodes
20 to maintain the potential difference between the sensing and reference electrodes at a fixed value, V_a . Depending upon the electrode configuration, three possible sensing modes are possible:

Firstly the active and inert sensing electrodes may be formed from
25 catalytically dissimilar materials. The active electrode may, for example, be formed from platinum and the inert electrode from gold. In use the current, I_i , flowing between the reference and inert sensing electrode mirrors that between the reference and active sensing electrode, I_a , and the potential difference between the two sensing electrodes is measured.

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Secondly the current I_i may be a sub-unit multiple of or equal to the current, I_a , flowing between the reference and active sensing

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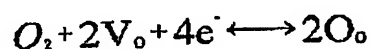
electrode and the potential difference between the two sensing electrodes is again measured.

Finally, the active and inert sensing electrodes may be formed from catalytically similar materials, such as platinum, for example. In this case the current flowing between the reference and inert sensing electrodes is a sub-unit multiple of the current, I_a , flowing between the reference and active sensing electrodes and the potential difference between the two sensing electrodes is again measured.

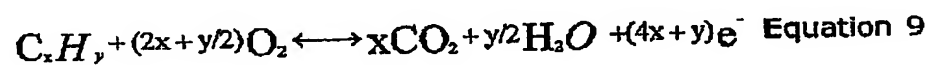
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In all cases the potential difference between the active and inert sensing electrodes will depend upon the positions of the mixed potential present on the electrode surface. The mixed potential, for a particular electrode surface, arises from the catalytic competition between the electrochemical reduction of oxygen and the oxidation or combustion of the organic material arriving at the electrode surface.

15



Equation 7



Equation 9

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Where V_o is a doubly charged oxygen anion vacancy and O_o is a filled oxygen anion site in the oxygen anion conducting solid state conductor. Pumping oxygen to the electrode surface (the reverse of equation 7) has a beneficial effect in that it allows the combustion reaction to take place in an oxygen depleted process environment.

25

The sensor is also easy to use and can be used at the point of use rather than the point of entry to provide accurate information about the process environments at all stages of the semi-conductor fabrication process.

30

The total level of contaminants measured by the sensor of the first aspect of the invention provides a semi-quantitative indication of the level of harmful organic contaminants present in the process environment. The non-contaminating light organic molecules present in the process environment do not stick to the surface of the measurement electrode and are not therefore measured. It is only the harmful organic contaminants, which have a high reaction probability with the electrode surface (and therefore with other surfaces encountered in the fabrication process) that undergo dissociation at and are therefore subsequently oxidised at the measurement electrode surface that are detected and therefore monitored by the measurement electrode.

Careful choice of the coating applied to the active sensing electrode or the material from which it is formed will cause some of the harmful organic contaminants to adsorb onto the surface of the measurement electrode in preference to others. Preferably the measurement electrode is formed from material whose uptake of organic material proceeds with a sticking probability of or about unity. In addition the organic material is preferably efficiently adsorbed and cracked by electrode material. Suitable electrode materials include metals selected from the group comprising rhenium, osmium, iridium, ruthenium, rhodium, platinum and palladium and alloys thereof. Alloys of the aforementioned materials with silver, gold and copper may also be used.

The sensor according to the first aspect of the invention is easily and readily manufactured using techniques known to a person skilled in the art. Sensing, reference and optionally counter electrodes are applied to a thimble of an oxygen anion conductor solid state electrolyte such as yttria stabilised zirconia either in the form of an ink or a paint or using techniques such as sputtering. The sensing electrodes are isolated from the reference and optionally counter electrode via the formation of a gas tight seal. The sensor suitably supplied with heater means to control the temperature of the electrolyte and means to monitor the voltage between

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the sensing electrode and the reference and counter electrodes respectively.

The reference electrode is suitably formed from materials, which
5 are able to catalyse the dissociation of oxygen. Platinum electrodes are suitably used as reference electrodes. The reference environment can be derived from a gaseous or solid state source of oxygen. Typically atmospheric air is used as a gaseous reference source of oxygen although other gas compositions can be used. Solid State sources of oxygen
10 typically comprise a metal/metal oxide couple such as Cu/Cu₂O and Pd/PdO or a metal oxide/metal oxide couple such as Cu₂O/CuO. The particular solid state reference materials chosen will depend on the operating environment of the sensor.

15 The solid state electrolyte comprising an oxygen anion conductor is suitably formed from a material, which exhibits oxygen anion conduction at temperatures above 300°C. Suitable oxygen anion conductors include gadolinium doped ceria and yttria stabilised zirconia. Preferred materials for use as the solid state oxygen anion conductor include 3% and 8%
20 molar yttria stabilised zirconia (YSZ), both of which are commercially available.

A radiative heater is suitably used to control the temperature of the cell. Such heaters include heating filaments, wound around the solid state
25 electrolyte. An electric light bulb can also be used.

A thermocouple is suitably used to monitor the temperature of the cell.

30 Currents of between 10nA / cm² and 100 µA / cm² are suitably used for driving oxygen anions between the reference and active and inert sensing electrodes. Currents outside this range can be used, depending upon the circumstances. The absolute magnitude of the current used to

drive the oxygen anions between the reference and measurement electrodes depends upon the surface area of the sensing electrodes, the partial pressure of oxygen in the sensing environment and the quantities of organic contaminants to be sensed. Larger currents will generally be
5 required for environments which are oxygen free but have high levels of organic contaminants. The sensor is preferably used in conjunction with a device for measuring the potential (Electromotive Force, EMF) produced across the cell.

10 Although the sensor of the first aspect of the invention can be used with just three electrodes (the reference and two measurement electrodes) only, it is preferred to use an electrode arrangement comprising a counter electrode in addition to the measurement and reference electrodes as described above. The counter electrode is
15 positioned adjacent to the reference electrode and in contact with the same reference environment as the reference electrode. In this preferred embodiment, the currents I_a and I_i flows between the counter electrode and the active and inert sensing electrodes respectively. The reference electrode therefore provides a constant reference environment from which
20 the electrochemical potentials of both the measurement and counter electrodes and therefore the potential difference across the cell can be determined. The counter electrode is preferably formed from materials such as platinum which actively catalyse the dissociative adsorption of oxygen.

25

The dimensions of the top and bottom surfaces of the sensor are typically of the order of a few square centimetres. The electrodes formed or deposited on each of the surfaces are therefore dimensioned accordingly. The counter electrode is typically equal in surface area to the
30 sum of the sensing electrodes. The reference electrode is usually of a lesser dimension. The electrodes are typically between 0.1 and 50 microns thick.

It will be appreciated that the sensor of the first aspect of the invention can be used to monitor the levels of trace organic contaminants in process environments and a second aspect of the invention provides the use of the sensor according to the first aspect of the invention to
5 monitor levels of trace organic contaminants in process environments.

It will further be appreciated that the sensor of the first aspect of the invention can be used in a method for monitoring the level of trace organic contaminants in process environments. A third aspect of the
10 invention provides a method for monitoring the levels of trace organic contaminants in a monitored process environment, the method comprising the steps of providing an electrochemical sensor comprising:

a solid state oxygen anion conductor having a first and a second surface, wherein oxygen anion conduction occurs at or above a critical
15 temperature, T_c ;

an active measurement electrode formed on the first surface of said solid state oxygen anion conductor, the active measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the oxidation of an organic contaminant molecule to carbon
20 dioxide and water at the surface thereof, the electrode being positioned for exposure to the monitored environment;

an inert measurement electrode formed on the first surface of the solid state oxygen anion conductor adjacent to and independent of the active measurement electrode, the inert measurement electrode being
25 coated with or formed from a material, which is catalytically inert to the oxidation of an organic contaminant molecule at the surface the electrode being positioned for exposure to the monitored environment;

a reference electrode formed on the second surface of the solid state oxygen anion conductor, the reference electrode being coated with
30 (or comprised from) a catalyst selected for its ability to catalyse the dissociative adsorption of oxygen, the reference electrode being positioned within a reference environment;

means for controlling and monitoring the temperature of the cell at

a temperature at or above the critical temperature, T_c , of the oxygen anion conductor;

sealing means for separating the reference environment from the monitored environment;

- 5 means for controlling the electrical currents, I_a and I_i , flowing between the reference electrode and the active and inert measurement electrodes respectively, thereby to control the flux of oxygen anions flowing between the reference electrode and the active and inert measurement electrodes respectively; and
- 10 means for monitoring the potential difference, V_{sense} between the active measurement electrode (E_a) and the inert electrode (E_i) exposing the active and inert sensing electrodes to the monitored process environment containing one or more organic contaminant species whereby the one or more organic contaminant species are adsorbed onto and
- 15 oxidised at the surface of the active sensing electrode and monitoring the potential difference V_{sense} between the active and inert sensing electrodes thereby to determine the amount of organic contaminants present in the process environment.

- 20 As indicated above the use of a sensor having reference, counter and measurement electrodes is preferred to optimise the electrical stability across the cell. Therefore, in a second preferred embodiment of the third aspect of the invention there is provided a sensor having, in addition to the reference and measurement electrode as described above,
- 25 a counter electrode positioned adjacent to the reference electrode and in contact with the same reference environment as the reference electrode. In this preferred embodiment, the currents I_a and I_i flow between the counter electrode and the measurement electrode. The reference electrode therefore provides a constant reference environment from which
- 30 the electrochemical potentials of both the measurement and counter electrodes and therefore the potential difference across the cell can be determined.

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The invention will now be described with reference to the following figures and examples in which:

Figure 1 illustrates an embodiment of a sensor according to the first aspect of the invention.

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Variations on these examples falling within the scope of the current invention will be apparent to a person skilled in the art.

The electrochemical sensor 1 of figure 1 comprises an active
10 sensing electrode 2 made of platinum and inert sensing electrode 3 made
of gold deposited on the upper (sensing) surface 4 of a solid state
electrolyte 5 comprising an 8% yttria stabilised zirconia oxygen anion
conductor using techniques such as vacuum sputtering or applying a
suitable commercially available "ink" to the surface, for example. In the
15 event that the electrode is formed on the surface of the sensor using an
ink, the whole assembly must be fired in a suitable atmosphere
determined by the nature of the ink. A platinum reference electrode 6 is
formed on the under surface 7 of the electrolyte 5 along with a counter
electrode 12. The reference electrode is formed on the under surface of
20 the electrolyte 5 using similar techniques to those described above. The
reference electrode 6 is placed in contact with a reference environment 8,
which may be either a gaseous source of oxygen at constant pressure
(such as atmospheric air) or a solid-state source of oxygen, typically a
metal/metal oxide couple such as Cu / Cu₂O and Pd / PdO or a metal
25 oxide/metal oxide couple such as Cu₂O / CuO. The sensor is typically
mounted in the environment to be monitored using a mounting flange 9
and the measurement electrodes 2,3 are typically isolated from the
reference environment 8 through the use of gas tight seals 10a, 10b. In
this way it is possible to separate the environment to be monitored from
30 the reference environment 8 and the reference electrode 6. The solid
state electrolyte 5 is provided with a heater and thermocouple
arrangement 11 to control the temperature of the sensor. The heater
and/or thermocouple may be bonded to the electrolyte prior to the

formation of the electrodes; sputtered onto the electrolyte subsequent to the formation of the electrodes or wound round the electrolyte prior to or subsequent to the isolation of the sensing electrodes from the reference environment.

5

A current source arrangement is also provided to control the current flowing from the reference electrode to the measurement electrodes. A voltammeter is also provided to measure the potential difference across the cell.

10

In use, the upper surface of the sensor 1 and therefore the measurement electrodes 2 and 3 are exposed to an environment to be monitored, including any organic contaminants. Organic material is absorbed onto and combusted at the surface of the active sensing electrode due to its reaction with oxygen species pumped to the surface of the active sensing electrode due to current I_a . The concentration of oxygen species at the surface of the active electrode is therefore diminished by its reaction with the organic contaminant species present. Since little or no combustion of the organic contaminant occurs at the surface of the inert sensing electrode, the electrochemical potential measured at that electrode is a reflection of the concentration of oxygen species present at the surface of that electrode as a result of the application of the current I_i and also the intrinsic (low) concentration of oxygen present in the process environment. The measured potential difference between the active and inert sensing electrodes therefore provides an indication of the amount of oxygen consumed by the organic contaminant at the surface of the active sensing electrode and therefore the concentration of organic contaminants in the process environment.

30 Example

Construction of the Sensor

Reference, sensing and optionally counter electrodes were formed on a thimble / disc of the oxygen anion conducting electrolyte

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(commercially available from various suppliers) by sputtering under vacuum or using commercially available 'inks' and firing the assembly in a suitable atmosphere according to the procedure given by the ink manufacturer.

5

A gas tight seal (resistant to both vacuum and pressure) was formed around the oxygen anion conducting electrolyte to isolate the sensing electrode from the reference electrode and optionally counter electrode using standard procedures. Depending upon how the sensor is
10 to be heated the heater / thermocouple can be added at any appropriate stage during manufacture.

The previously described embodiments of the sensor relate to the detection of organic contaminant species in oxygen deficient
15 environments. Under atmospheres containing significant levels of oxygen (partial pressures $> 2.0 \cdot 10^{-1}$ mb i.e. $> 0.1\%$) as may be found in the exhaust gases from internal combustion engines, for example, oxygen is no longer needed to be pumped to the sensing electrodes to enable the combustion reactions to take place and thereby develop the mixed
20 potential - the oxygen is provided via gas phase adsorption.

However, it is widely known (Vayenas et al, Catalysis Today vol. 11 (1992) pp 303-442) that under such conditions the catalytic properties of electrodes can be modified by pumping quantities of oxygen to the surface of the electrodes, currents typically in the range 1 microamp/cm^2 - 1
25 milliamp/cm^2 . This Non Faradaic Electrochemical Modification of Chemical Activity is known as the NEMCA effect. Here the oxygen anions pumped to the surface of the electrodes do not take place in the combustion reactions directly but rather act as promoters for the heterogeneous combustion of the organic contaminant species by gas phase oxygen.
30 Thus by controlling the quantities of promoting oxygen anions at the surface, via the currents I_a and I_r , different rates of combustion will occur giving rise to different mixed potentials at the electrodes. This is in

contrast to the method in DE95/00255 where the dissimilar catalytic reactions and hence the mixed potentials are enhanced by operating the electrodes at different temperatures which is difficult to achieve practically.

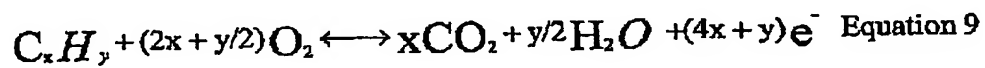
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The activation of the NEMCA effect increases the rate of combustion of organic contaminant at the surface of the active electrode and therefore reduces the overall response time and increases the sensitivity of the sensor.

10

In all cases the potential difference between the active and inert sensing electrodes will depend upon the positions of the mixed potential present on the electrode surfaces. The mixed potential, for a particular electrode surface, arises from the catalytic competition between the electrochemical reduction of oxygen and the oxidation or combustion of the organic material arriving at the electrode surface.

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Where V_o is a doubly charged oxygen anion vacancy and O_o is a filled oxygen anion site in the oxygen anion conducting solid state conductor. Pumping oxygen to the electrode surface (the reverse of equation 7) has a number of beneficial effects:

25

Firstly it increases the rate of the combustion reactions occurring at the electrode surface by virtue of the NEMCA effect. Catalytic reaction rates can be enhanced by a factor of up to 1000. This results in a faster and potentially bigger sensor response.

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Secondly, by pumping different amounts of oxygen to the electrodes the NEMCA effect can be controlled and different mixed potentials can be achieved on electrodes of the same material type.

5 The sensor construction for operation at high oxygen levels is identical to that for use in oxygen deficient environments save that solid state reference materials cannot be used due to the potentially high oxygen anion currents – the solid state reference material would become exhausted in a short period of time.

10

In use the sensor operates by passing an anion current, I_a (O^{2-}), between the reference electrode and one of the sensing electrodes to maintain the potential difference between the sensing and reference electrodes at a fixed value, V_a . Depending upon the electrode
15 configuration, three possible sensing modes are possible:

Firstly the active and inert sensing electrodes may be formed from catalytically dissimilar materials. The active electrode may, for example, be formed from platinum and the inert electrode from gold. In use the
20 current, I_i , flowing between the reference and inert sensing electrode mirrors that between the reference and active sensing electrode, I_a , and the potential difference between the two sensing electrodes is measured.

Secondly the current I_i may be a sub-unit multiple of or equal to
25 the current, I_a , flowing between the reference and active sensing electrode and the potential difference between the two sensing electrodes is again measured.

Finally, the active and inert sensing electrodes may be formed from
30 catalytically similar materials, such as platinum, for example. In this case the current flowing between the reference and inert sensing electrodes is a sub-unit multiple of the current, I_a , flowing between the reference and

24.

active sensing electrodes and the potential difference between the two sensing electrodes is again measured.

- 5 For operation in atmospheres containing significant levels of oxygen (partial pressures $> 2.0 \cdot 10^{-1}$ mb i.e. $> 0.1\%$) the third electrode configuration listed above will be preferred - for operation in oxygen deficient environments the first electrode configuration is preferred.

10

Claims

1. An organic contaminant molecule sensor, for use in a low oxygen concentration monitored environment the sensor comprising an electrochemical cell having:
- 5 a solid state oxygen anion conductor having a first and a second surface, wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;
- 10 an active measurement electrode formed on the first surface of said solid state oxygen anion conductor, the active measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the oxidation of an organic contaminant molecule to carbon dioxide and water at the surface the electrode being positioned for exposure to the monitored environment;
- 15 an inert measurement electrode formed on the first surface of the solid state oxygen anion conductor adjacent to and independent of the active measurement electrode, the inert measurement electrode being coated with or formed from a material, which is catalytically inert to the oxidation of an organic contaminant molecule at the surface the electrode being positioned for exposure to the monitored environment;
- 20 a reference electrode formed on the second surface of the solid state oxygen anion conductor, the reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociative adsorption of oxygen, the reference electrode being positioned within a reference environment;
- 25 means for controlling and monitoring the temperature of the cell at a temperature at or above the critical temperature, T_c , of the oxygen anion conductor;
- 30 sealing means for separating the reference environment from the monitored environment;

means for controlling the electrical currents, I_a and I_i , flowing between the reference electrode and the active and inert measurement electrodes respectively, thereby to control the flux of oxygen anions flowing between the reference electrode and the active and inert measurement electrodes respectively; and

means for monitoring the potential difference between the active measurement electrode (E_a) and the inert electrode (E_i) whereby in the absence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes assumes a base value V_b and in the presence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes assumes a measurement value V_m , the value $V_m - V_b$ being indicative of the concentration of organic contaminant molecules present in the monitored environment.

2. A sensor according to claim 1, wherein the measurement electrode is coated with or formed from an element selected from the group comprising rhenium, osmium, iridium, ruthenium, rhodium, platinum and palladium and alloys thereof.
3. A sensor according to claim 2, wherein the alloys used further include alloys including one or more elements selected from silver, gold and copper.
4. A sensor according to any one of claims 1 to 3, wherein the reference electrode is able to catalyse the dissociation of oxygen.
5. A sensor according to claim 4, wherein the reference electrode is platinum.

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6. A sensor according to any one of the preceding claims, wherein the solid state oxygen anion conductor is selected from gadolinium doped ceria and yttria stabilised zirconia.
- 5 7. A method according to any one of the preceding claims wherein the reference oxygen environment is a solid-state source of oxygen typically from a metal / metal oxide couple such as Cu / Cu₂O and Pd / PdO or a metal oxide / metal oxide couple such as Cu₂O / CuO.
- 10 8. A sensor according to any one of the preceding claims, which further comprises a counter electrode, said counter electrode being positioned adjacent to the reference electrode.
9. A sensor according to claim 8, wherein the counter electrode is composed of platinum.
- 15
11. A sensor according to any one of the preceding claims, wherein the means for controlling or monitoring the temperature of the cell comprises a heater and thermocouple arrangement.
- 20
12. Use of a sensor according to any one of claims 1 to 10 for monitoring the levels of trace organic contaminants in a low oxygen concentration monitored process environment.
- 25 13. A method for monitoring the levels of trace organic contaminants in a monitored process environment, the method comprising the steps of providing an electrochemical sensor comprising:
- a solid state oxygen anion conductor having a first and a second surface, wherein oxygen anion conduction occurs at or above a critical temperature, T_c;
- 30 an active measurement electrode formed on the first surface of said solid state oxygen anion conductor, the active measurement electrode being coated with (or formed from) a catalyst having the

ability to catalyse the oxidation of an organic contaminant molecule to carbon dioxide and water at the surface the electrode being positioned for exposure to the monitored environment;

5 an inert measurement electrode formed on the first surface of the solid state oxygen anion conductor adjacent to and independent of the active measurement electrode, the inert measurement electrode being coated with or formed from a material, which is catalytically inert to the oxidation of an organic contaminant molecule at the surface thereof the electrode being
10 positioned for exposure to the monitored environment;

a reference electrode formed on the second surface of the solid state oxygen anion conductor, the reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociative adsorption of oxygen, the reference
15 electrode being positioned within a reference environment;

means for controlling and monitoring the temperature of the cell at a temperature at or above the critical temperature, T_c , of the oxygen anion conductor;

20 sealing means for separating the reference environment from the monitored environment;

means for controlling the electrical currents, I_a and I_i , flowing between the reference electrode and the active and inert measurement electrodes respectively, thereby to control the concentration of oxygen anions flowing between the reference
25 electrode and the active and inert measurement electrodes respectively; and

means for monitoring the potential difference between the active measurement electrode (E_a) and the inert electrode (E_i) exposing the active and inert sensing electrodes to the monitored process environment containing one or more organic contaminant species whereby the one or more organic contaminant species are adsorbed onto and oxidised at the surface of the active sensing
30 electrode and monitoring the potential difference V_s between the

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active and inert sensing electrodes thereby to determine the amount of organic contaminants present in the process environment.

- 5 14. A method according to claim 13, wherein the current I_p passing between the reference and measurement electrode is in the range 10nA to 100 μ A.
- 10 15. A method according to claim 13 or claim 14, wherein the sensor is further provided with a counter electrode adjacent to the reference electrode.
- 15 16. An organic contaminant molecule sensor for use in environments having high oxygen concentrations, the sensor comprising an electrochemical cell having:
- an oxygen anion conductor wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;
- an active measurement electrode in contact with the oxygen anion conductor, the active measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the
- 20 oxidation of an organic contaminant molecule to carbon dioxide and water at the surface the electrode being positioned for exposure to the monitored environment;
- an inert measurement electrode in contact with the oxygen anion conductor independent of the active measurement electrode,
- 25 the inert measurement electrode being coated with or formed from a material, which is catalytically inert to the oxidation of an organic contaminant molecule at the surface the electrode being positioned for exposure to the monitored environment;
- a reference electrode in contact with the oxygen anion conductor, the reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociative
- 30

30

adsorption of oxygen, the reference electrode being positioned within a reference environment;

means for controlling and monitoring the temperature of the cell at a temperature at or above the critical temperature, T_c , of the oxygen anion conductor;

sealing means for separating the reference environment from the monitored environment;

means for controlling the electrical currents, I_a and I_i , flowing between the reference electrode and the active and inert measurement electrodes respectively, thereby to control the flux of oxygen anions flowing between the reference electrode and the active and inert measurement electrodes respectively such that the NEMCA effect is activated; and

means for monitoring the potential difference between the active measurement electrode (E_a) and the inert electrode (E_i) whereby in the absence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes assumes a base value V_b and in the presence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes assumes a measurement value V_m , the value $V_m - V_b$ being indicative of the concentration of organic contaminant molecules present in the monitored environment.

ABSTRACT
Electrochemical Sensor

5 An organic contaminant molecule sensor 1, for use in a low oxygen concentration monitored environment the sensor comprising an electrochemical cell having:

 a solid state oxygen anion conductor 5 having a first 4 and a second 7 surface, wherein oxygen anion conduction occurs at or above a
10 critical temperature, T_c ;

 an active measurement electrode 2 formed on the first surface 4 of said solid state oxygen anion conductor, the active measurement electrode 2 being coated with (or formed from) a catalyst having the ability to catalyse the oxidation of an organic contaminant molecule to
15 carbon dioxide and water at the surface the electrode being positioned for exposure to the monitored environment;

 an inert measurement electrode 3 formed on the first surface 4 of the solid state oxygen anion conductor adjacent to and independent of the active measurement electrode 2, the inert measurement electrode 3 being
20 coated with or formed from a material, which is catalytically inert to the oxidation of an organic contaminant molecule at the surface the electrode being positioned for exposure to the monitored environment;

 a reference electrode 6 formed on the second surface of the solid state oxygen anion conductor, the reference electrode being coated with
25 (or comprised from) a catalyst selected for its ability to catalyse the dissociative adsorption of oxygen, the reference electrode 6 being positioned within a reference environment 8;

 means for controlling and monitoring the temperature of the cell at a temperature at or above the critical temperature, T_c , of the oxygen anion
30 conductor;

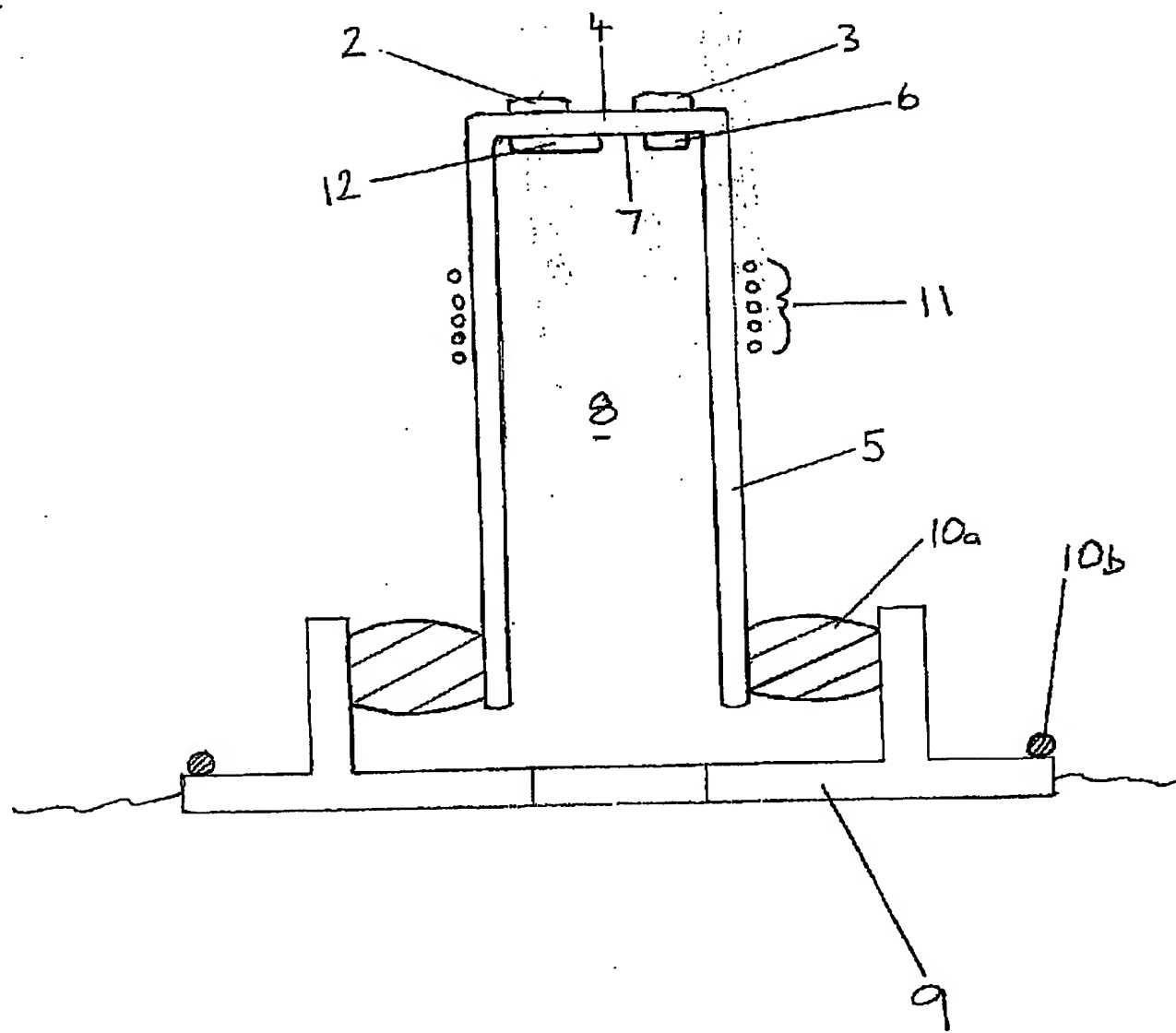
 sealing means 10a, 10b for separating the reference environment 8 from the monitored environment;

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means for controlling the electrical currents, I_a and I_i , flowing between the reference electrode 6 and the active and inert measurement electrodes 2,3 respectively, thereby to control the flux of oxygen anions flowing between the reference electrode 6 and the active and inert measurement electrodes 2, 3 respectively; and

means for monitoring the potential difference between the active measurement electrode (E_a) and the inert electrode (E_i) whereby in the absence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes 2,3 assumes a base value V_b and in the presence of organic contaminant molecules the potential difference V_{sense} between the active and inert measurement electrodes 2,3 assumes a measurement value V_m , the value $V_m - V_b$ being indicative of the concentration of organic contaminant molecules present in the monitored environment.

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FIG. 1

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